Low-Temperature Migration of Silicon in Metal Films on Silicon Substrates Studied by Backscattering Techniques*

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The backscattering method using 2-MeV $^4He^+$ ions is employed to obtain microscopic information about solid–solid reaction of Si with thin layers (200~4000 Å) of Au, Ag, and Al which are vacuum evaporated onto Si crystal substrates. The interesting observation is the migration of Si atoms into these metal films at temperatures (for example, 150°C in Au, 400°C in Ag) well below their eutectic points (375°C for Au and 850°C for Ag). This phenomenon also indicates that at these low temperatures the dislodgment of Si atoms from tightly bound Si crystal does occur. Our experiments clarify that the origin of this effect is the interaction of Si with metals at the interface.

Introduction

Backscattering measurements using MeV He ions provide information about the identification and depth distribution of impurities as well as atomic composition of the target material. Using this technique, our previous work[1] indicated that, when a silicon crystal covered with gold of thickness ranging from 200 to 4000 Å was heated in air to about 200°C, the accumulation of silicon atoms in the form of silicon dioxide (SiO_2) took place on top of gold surface.

This phenomenon is interesting from the point that at this low temperature silicon atoms are dislodged from the tightly bound silicon cyrstal to migrate through the gold film.

For the study of this effect the backscattering method is particularly useful because it enables one to see in a nondestructive manner what is happening at the surface and at depths down to about 10 000 Å from the surface of the specimen.

I. Analysis: Principle of Backscattering Technique

The experimental setup and the principle of analysis have been described elsewhere[2–4] and will be simply summarized here for the reader's convenience. A collimated beam of high-energy $^4He^+$ ions strikes the specimen mounted on the target holder. The backscattered particles are detected by a semiconductor nuclear particle detector. A brief sketch of the system is given at the top of Fig. 1. Energy analysis of the scattered particles gives

(*1*) *Mass determination of atoms* located on the specimen surface. From the energy E' of the He^+ particle backscattered from the target, one can de-

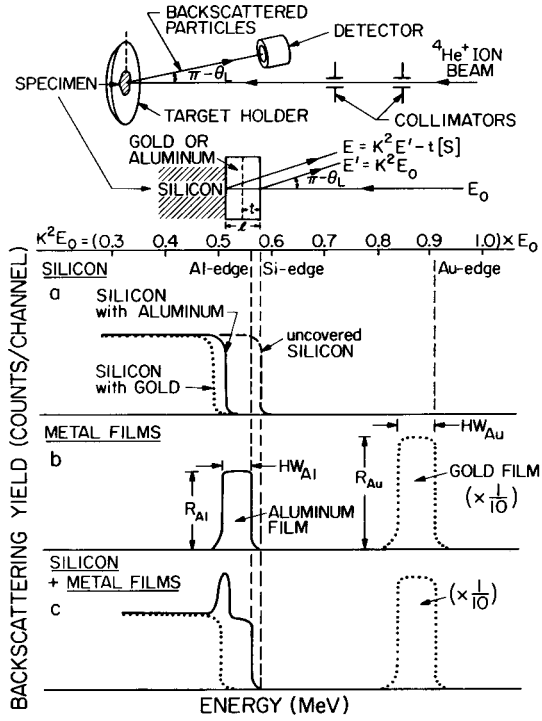

FIGURE 1. Schematic scattering geometry (above) and backscattering energy spectra generated from targets of (a) silicon substrates under the metal films, (b) metal films, and (c) metal films overlying silicon.

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termine the mass M_2 of the target atom. The energy E' is given in terms of incident energy E_0 and mass M_1 of incident particle, mass M_2 of the target atom and backscattering angle θ_L (which is fixed by the detector geometry in the laboratory system of coordinates) by

$$E' = K^2 E_0,$$

where

$$K^2 = \left\{ \frac{M_1 \cos\theta_L}{M_1+M_2} + \left[\left(\frac{M_1 \cos\theta_L}{M_1+M_2} \right)^2 + \frac{M_2 - M_1}{M_1+M_2} \right]^{\frac{1}{2}} \right\}^2.$$

(2) *Depth distribution of atoms.* The measured energy of He^+ particles backscattered at a depth t below the surface is lower than that of particles scattered from atoms on the surface. This is due to the energy loss of the particle in penetrating the specimen to depth t and in exiting. Since energy loss is readily calculated from the data on stopping power accumulated in the field of nuclear physics, it is possible to convert backscattering spectra from energy to depth scales to obtain the depth distribution of atoms.

(3) *Number of atoms* is proportional to the area under the spectrum of corresponding atoms. From the knowledge of scattering cross section and stopping power of the target atom, the conversion of scattering yield to atomic concentration is obtained.

To illustrate the above-mentioned features, the schematic representation of the backscattering spectra of two silicon wafers covered with either aluminum or gold films with the same thickness l are given in Fig. 1. He^+ particles with incident energy E_0 are scattered from atoms Al or Au on the surface, through an angle θ_L into detector, with energy K^2E_0, while the particles scattered from atoms at depth t below the surface have energy $K^2E_0 - t[S]$. $[S]$ is called the backscattering energy loss parameter[3] (or $[S]$ factor) which relates the energy to the depth scale;

$$[S] \simeq K^2 \left.\frac{dE}{dx}\right|_{E_0} + \frac{1}{|\cos\theta_L|} \left.\frac{dE}{dx}\right|_{K^2E_0},$$

where dE/dx is stopping power of the target material (Al or Au).

The spectra of both aluminum and gold films are shown in Fig. 1(b), respectively, by solid and dotted profiles. Although the thicknesses of both films are the the same, their widths at half-height of the spectra HW_{Al} and HW_{Au} are different because of the different values of the $[S]$ factor for Al and Au. The scattering yields of the films R_{Al} and R_{Au} are proportional to atomic concentration, scattering cross section and inverse $[S]$ factor ($1/[S]$) of Al and Au. The spectra of thick wafers of silicon covered with aluminum or gold films (solid or dashed lines) are shifted to lower energies from the spectrum of uncovered silicon (dashed lines) as shown in Fig. 1(a). The larger shift of the spectrum of silicon with Au film comes from the larger stopping power of Au than Al which produces a larger energy loss for He^+ particles in traversing in the gold film. The superposition of Figs. 1(a) with 1(b) gives the actual spectra 1(c) of the specimens: solid line for Si–Al and dotted line for Si–Au. In contrast with the Si-Au case whose resultant spectrum is simple, the spectrum of Si–Al is characterized by a sharp peak which is due to particles scattered by Si and Al at the interface. Before heat treatments, the sharpness of this peak follows the well-defined nature of the Si/Al interface. This suggests the study of the interface versus heat treatments by observing the change in this peak.

II. Experimental

Silicon wafers with surface orientation of either {110} or {111} were prepared by conventional mechanical and chemical polishing, after which the specimens were kept in diluted hydrofluoric acid to prevent surface oxidation until just before the evaporation of aluminum, gold or silver. The evaporations were done in a vacuum of about 5×10^{-7} Torr, and the film thickness ranged from 200 to 4000 Å. Immediately after the evaporations the adherences of the films to silicon substrates were tested using "Scotch" tape. Sometimes the films showed weak adherence and these specimens were not used for the experiments. Heat treatments of these metal-evaporated specimens were made under several different conditions; typically ambients of air, O_2 or steam. Then the backscattering data of these treated and untreated (as evaporated) specimens were taken using a 2-MeV $^4He^+$ beam from the 3-MV Van de Graaff accelerator of the Kellogg Radiation Laboratory at the California Institute of Technology.

III. Results and Discussion

When a gold-evaporated silicon wafer (Si–Au) was heated in air at about 200°C, the following facts[1] were deduced from backscattering spectra: (1) Silicon atoms migrate through the gold film and accumulate on its front surface. This was inferred by the presence of a peak in the spectrum (shown in Fig. 2) corresponding to silicon atoms on the surface (Si edge). (2) These silicon atoms are oxidized and form a SiO_2 layer which was also detected by the change in the color of the surface. Its composition ratio (Si:O = 1:2) can be obtained by the analysis[3] of both spectra at Si and O edges. Once a Si or SiO_2 layer is formed on top of gold, the backscattering spectrum of the gold film shifts to lower energy than before, due to the energy loss of He^+ particles in traversing the

oxide layer. From the slope of the leading edge of the shifted gold spectrum one can tell that the oxide layer is not uniform. (3) The growth rate of the oxide layer increases with increasing temperature of the heat treatment.

The above facts are important because the temperature at which these phenomena take place is well below the eutectic temperature (370°C) of the Si–Au system and therefore this process is referred to as "*Low-Temperature* Silicon Migration."

Similar effects of low-temperature silicon migration were also found in the systems of Si–Ag[5] and Si-Al[6] at 400° and 300°–350°C whereas their eutectic points are at 839° and 580°C, respectively. To understand this low-temperature migration and difference in migration temperature between our various systems, one should establish whether this phenomenon is limited by silicon transport through the metal film [mechanism (i)] or by silicon dislodgment at the silicon-metal interface [mechanism (ii)]. In order to answer this problem, a double-layer specimen of Si–Au–Ag was prepared by successive evaporations of gold and silver on silicon substrate. At 200°C, in the Si–Au–Ag system, silicon atoms are expected to move readily through the gold layer toward the Au/Ag interface. If the higher temperature (400°C) silicon migration in Si–Ag system comes from mechanism (i),

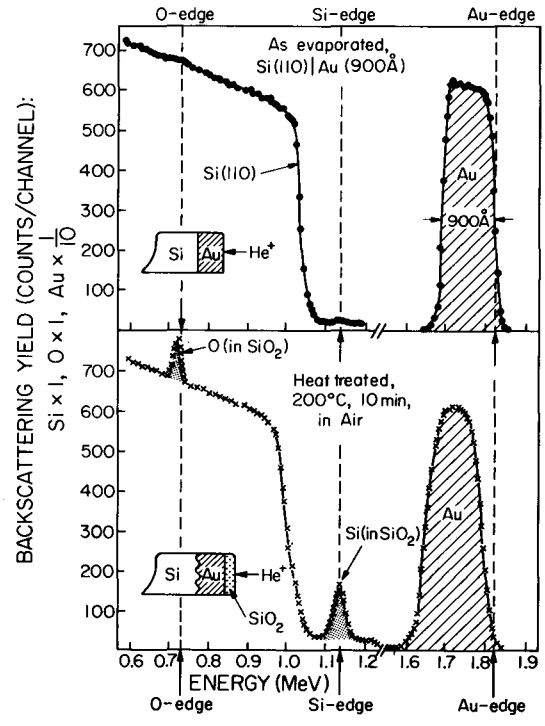

FIGURE 2. Energy spectra of 2-MeV $^4He^+$ ions backscattered from a randomly oriented silicon (110) wafer covered with 900 Å before (upper)—the shift of the leading edge of silicon spectrum is less than the width of the gold spectrum due to the difference in [*S*] factors—and after (lower) the heat treatment at 200°C in air for 10 min. Diffused Si/Au interface after the treatment is denoted by curved line.

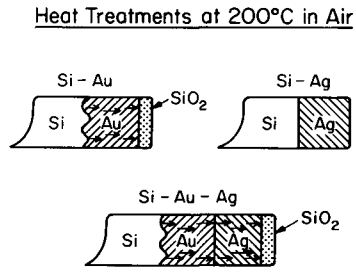

FIGURE 3. Schematic representations of the heat treatments at 200°C, in air of Si–Au, Si–Ag, and Si–Au–Ag systems. Curved lines represent the diffused Si/metal interface, while the straight lines the well-defined interface. Arrows indicate the migration of Si atoms.

due to higher activation energy of silicon transport through the silver layer, the silicon atoms should accumulate at the Au/Ag interface; however, if it is originated in mechanism (ii) due to higher threshold energy for silicon dislodgment at Si/Ag interface, some silicon accumulation on top of silver might be observed. The analysis[5] of the backscattering spectrum after the heat treatment of the specimen, indicates as described schematically in Fig. 3, that in the double layer sample SiO_2 formation on top of silver occurs at 200°C.[7] This fact suggests that mechanism (ii) is more probable. Also, the silver layer is expected to be reasonably similar to the gold layer for silicon transport, especially at 200°C where grain boundary diffusion is possibly the transport mechanism. In Si–Ag–Au system, on the other hand, silicon accumulation is not observed at the gold surface until 400°C which also suggests silicon dislodgment is the rate determining process.

Therefore we propose that the limiting process is related to the dislodgment of silicon at the silicon-metal interface.

The importance of this interface interaction is inferred also by the following observations:

(a) When the adherence of the evaporated film to the substrate is weak, the low-temperature migration is not observed. For example, silicon wafers slightly oxidized is hot nitric acid show a weak adherence to the evaporated gold films and an anneal of such specimens at temperatures as high as 300°C induce little, if any, SiO_2 layer on top of the gold layers.

(b) Crystallographic orientation of the silicon substrate has a marked influence on the rate of silicon accumulation. Oxide growth on gold films is more rapid with a {110} interface than with a {111}. Similar orientation effects[8] exist in thermal-oxidation processes and in chemical etching of silicon crystals, both of which are understood in terms of an interface reaction of silicon with the reacting species.

(c) The silicon-metal interface after heat treatment is not as well defined as before the treatment which is readily detected in Si–Al system treated above 300°C through the change in the peak corresponding to Si/Al interface from the reason stated already in Sec. I, suggesting that the reaction at the interface

induces *intermixing* of the metal with silicon where the original interface was located. This effect of interdiffusion of both materials is also clearly visible in a gold evaporated specimen which is heated at higher temperature (250°C for 10 min) or for longer time (200°C for 2 hr) to produce a thick (~2000 Å) oxide layer on gold.

Besides the above-mentioned study, the oxide formation observed in the Si–Au system is interesting since the temperature (100–200°C) is much lower than the ordinary thermal oxidation of silicon crystal which is above 700°C. The growth of the oxide at fixed temperature (say 200°C) follows a parabolic relation [$\propto (\text{time})^{\frac{1}{2}}$] suggesting that the oxidizing species diffuse through the already grown oxide. More rapid growth was observed in steam than in pure oxygen (O_2) atmosphere which supports the above suggestion, since the extrapolation of diffusivities[9] of both H_2O and O_2 molecules in amorphous SiO_2 to low temperatures indicates that the water molecules should be more diffusive at 200°C.

In summary, we are now confident that the low-temperature silicon migration originates in the interface interaction of silicon with metal. This might be related to the interactions which give rise to the eutectic liquid states in our Si–Ag, Si–Al and Si–Au systems, all of which are simple eutectic type. A detailed paper on the mechanism of oxide formation is to be published soon.

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